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Abstract

# CHEMISTRY OF SEPARATION OF PLUTONIUM FROM IRRADIATED FUEL

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The extraction of uranium, plutonium and mixed fission products from simulated solution of irradiated fuel by tri-n-butyl phosphate (TBP) in locally available kerosene as diluent has been studied with a view to collecting data for the design of a spent fuel reprocessing plant. The distribution coefficients for the above at different concentrations of TBP in kerosene have been determined as a function of nitric acid concentration in the aqueous phase and of the degree of saturation of the solvent phase with uranium. The data are presented in a graphical form along with the distribution coefficients for specific fission products like ruthenium and zirconium. The general trend of the results obtained, with locally available kerosene diluent, is the same as that of some other published work done under similar conditions, but differences in actual values of the distribution coefficients have been observed and the new data obtained for the distribution coefficients with respect to the degree of saturation of uranium at different concentration of TBP in the solvent phase could not be compared.

The final purification of plutonium by fixed-bed ion exchange has been investigated with three different types of resins, viz. Deacidite FF, Amberlite IRA-400 and Dowex-I x 4 with a view to establish the optimum conditions. The variation of the distribution coefficients as a function of nitric acid concentration for both uranium(VI) and plutonium(IV) in the case of Deacidite FF and Amberlite IRA-400 and distribution coefficients of solvent extracted fission products

with Dowex-I x 4 have been obtained. Absorption, break-through and elution behaviour in a column maintained at 60°C and at room temperature, have been examined. In the case of Dowex-I x 4, build-up of plutonium in the resin column due to repeated cycles of operation, has been determined and the decontamination of plutonium from fission products was found out after loading the column to three-fourth of its capacity under optimum conditions.

The mechanism of extraction of plutonium in hexone, butex and TBP has been studied by determining the distribution coefficients of plutonium by varying the nitrate ion and the hydrogen ion concentrations. From the extraction equilibria, it appears that plutonium extracts as $Pu(NO_3)_4$ from the aqueous phase into hexone and butex; but in the organic phase at higher acidity, $Pu(NO_3)_4$ changes into $H_2Pu(NO_3)_6$. Spectral changes in the organic phase in the visible range confirm these results. In TBP, plutonium nitrate is extracted as $Pu(NO_3)_4.2TBP$ which has also been confirmed by the fact that there are no spectral changes observed when organic phase acidity is varied.

The values of stability constants for nitrate complexes of plutonium(IV) at various ionic strength, determined by solvent extraction method using TBP as solvent are presented. The stability constant for sulphate complexes have also been determined using competitive method, as during reprocessing sulphamate is used for separating plutonium.

In the present process plutonium is precipitated as its oxalate from the nitrate solution and calcined to its oxide for conversion to metal through its fluoride. The decomposition of oxalates have, therefore, been studied using thermogravimetric and differential thermal analysis (DTA) methods. The kinetic parameters viz. heat of reaction, energy of activation and order of reaction have been calculated from the DTA curves.